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REACTION OF SOIL SYSTEM TO “ACID RAIN” UNDER CONDITIONS OF A LABORATORY EXPERIMENT*

ABSTRACT: Soil acidification with a solution of sulphuric acid (pH = 3) has decreased the intensity of metabolic processes in soil and the decomposition rate of organic matter in acidified systems, although the soil pH has not decreased yet. Already 6 months after acidification nitrifying processes are inhibited, whereas organic matter content increases in fermentation litter, the pH of which decreases.

KEY WORDS: Laboratory experiment, soil acidification, soil respiration, decomposition of organic matter, nitrogen contents.

1. INTRODUCTION

The anthropogenic effect on ecological processes is becoming more frequently an object of many investigations, recently being of major interest for a number of research groups.

The soil is one of the significant biocoenotic components not easily deformed, but once there are deformations they are hard to reverse. They affect significantly the ecological processes both in soil and plant systems, whereas the decomposition process decides about the direction and intensity of energy and matter flow in soil.

This is why the effect of anthropopressure on decomposition has been lately investigated with such an interest. These studies show, amongst other things, that under conditions of the pressure of heavy industry decomposition is inhibited (Dodd and Lauenroth 1980, Grodziński and York 1981). The cause of it has not been yet fully explained, but many scientists claim that heavy metals

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are responsible (Coughtrey et al. 1979, Zieliński 1979, and others) as they cumulate frequently in the litter and in the humus layer (Jordan and Lechavalier 1975, Inman and Parker 1978).

However, it should be remembered that industrial emission is always a result of various chemical influences, and the final effect recorded by scientists may be the effect of synergic action of a number of factors.

At present one of the most common pollutants, being a background for other, is the emission of SO_2 causing the acidification of the environment. The acidification of natural environment is becoming a world-wide problem as it affects directly the structure of micro- and mesofauna and also its activity, and thus significantly the ecological processes.

Grodziński (1978), Leetham et al. (1980), Pilarska et al. (1981), amongst others, discuss the role of pressure of heavy industry on the structure of destruents. The activity of destruents under conditions of heavy industry pressure is a key to ecological mechanisms in thus changed environmental conditions. They condition the amount and quality of energy and matter put in motion for the ecosystem.

Two methods can be used to estimate this activity: by determining the numbers and quality of organisms or by determining their effect. Here, the latter method has been used, and the authors try to find out, whether a soil system can react to a 6-month sprinkling with acid rain, by determining the metabolic activity of soil, organic matter and nitrogen content in soil, and also by determining the decomposition rate by cellulose filter method. The studies have been conducted under conditions of a laboratory experiment, where the fall was simulated by regular watering of soil exposed with water acidified by sulphuric acid.

2. MATERIAL AND METHODS

The experiment has been conducted in containers of a surface area 39 × 78 cm, and 40 cm in height. The containers were filled with soil from a fallow near the pine wood, but without the sod. A 10 cm soil layer was used in the experiment. For the purpose of unification the soil was sieved through a net of a mesh size 5 mm. Considering the differentiation of soil material a relatively uniform material was obtained, but the hitherto existing structure had to be damaged. The soil was placed in 20 containers and watered 3 times a week; 1.5 l of distilled water per container — an equivalent of 45 mm of fall per month. This is the frequently occurring amount in central Poland. The experiment was conducted at +15°C. Each container had at the bottom two holes, through which the excess of fluid trickled out. After 3 months the soil in 10 containers was watered with the same amounts of water acidified by sulphuric acid of a pH 3. This is the acidity of rains in some industrial regions in Europe.

Among the 20 containers 10 were only with soil (5 watered with distilled water, 5 — with acidified water) and 10 with a layer of needle litter on the surface (5 watered with distilled water, 5 – with acidified water). The litter was sampled and spread in two layers: top layer A – undecomposed, bottom layer B – partly decomposed. From three containers of each series of 5 containers samples were taken, whereas the remaining two were subsidiary ones from which soil or litter were used to replace the material taken for analyses. Figure 1 illustrates the diagram of experiment.

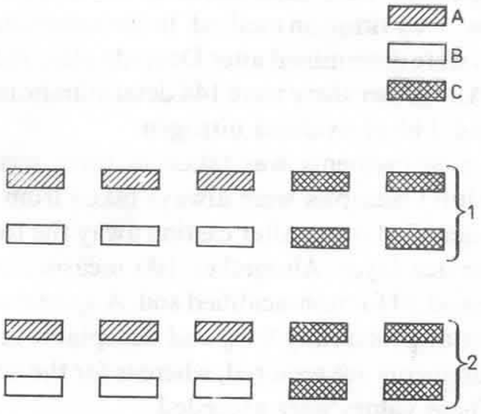

Fig. 1. Diagram of the experiment
A – containers with acidified soil, B – containers with soil sprinkled with distilled water, C – subsidiary containers, 1 – containers with uncovered soil, 2 – containers with soil and litter

Samples were taken at random; 1, 2.5 and 6 months after the acidification began. Samples for measuring the oxygen respiration were taken at slightly different dates because of technical reasons, i.e., after 2, 4, and 6 months.

The moisture, acidity, contents of organic matter and nitrogen compounds in soil and litter were measured. Total nitrogen, ammonia nitrogen and oxidized nitrogen compounds were considered as the ecologically most significant nitrogen compounds.

Also in indicatory investigations with cellulose filters attempts were made to determine the rate of organic matter decomposition in soil and the differences in metabolic activity of destruents using Kearney's medium.

The sulphate content in liquid trickling out of containers was determined.

The following methods were used:

(1) Weight method for moisture.

(2) Soil and litter acidity were determined in a water solution 1:1 by a universal pH-meter using glass and kalomel electrodes.

(3) Organic matter in soil and litter was determined by combustion at 500°C (data provided by Z. Olszewski, M.Sc.).

(4) Decomposition rate was measured by an indicatory method, where in all variants paper filters were buried in a 0–5 cm soil layer during the first three months (I–III) and for the next three ones (IV–VI). In the first variant (I–III) there were 18 filters in each acidified and non-acidified container, altogether 72; in the next one (IV–VI) there were 9 in each, altogether 36.

(5) The content of sulphates trickling out of containers was measured by a gravimetric method as barium sulphate (data obtained by Dr. A. Dowgiałło).

(6) Out of nitrogen compounds determined were total nitrogen, ammonia nitrogen and oxidized nitrogen compounds. Total nitrogen samples were mineralized after Kjeldahl and then determined according to the expected amount of N or by indophenol method of ammonia determination, or by Nessler's method (Dowgiałło 1984). Oxidized nitrogen compounds were determined in the distillate of soil extract in a solution KCl 1 mole · dm $^{-3}$ by titration method. In the same sample oxidized nitrogen compounds (NO_2, NO_3) were determined after Deverda alloy reduction (Kropisz and Starck 1981). Altogether there were 144 determinations of total nitrogen, 144 of ammonia nitrogen and 144 of oxidized nitrogen.

Soil for respiration measurements was taken in three series in winter (March), spring (May), summer (July). Samples were always taken from 6 containers – three acidified and three non-acidified ones. After casting away the top 5 mm layer samples were taken from the surface layer. Altogether 100 measurements of respiration of acidified soil were made and 80 for non-acidified soil. A special series of measurements allowed to calculate that at probability 95% and acceptable scatter 5% for the non-acidified series 57 measurements are required, whereas for the acidified series, having a greater scatter – 87. These values were exceeded.

Oxygen consumption by soil was measured by a modified volumetric respirometer (Klekowski 1975). Into each container 7 g of wet soil weight was put, i.e., about 4 g dry weight. A 4 ml Kearney's solution with 5% glucose was poured on soil in the container and measurements were made at 20°C after 24-hour incubation. Kearney's medium consisted of: 1.2 g K_2HPO_4, 0.3 g KH_2PO_4, 0.2 g $MgSO_4 \cdot 7$ aq, 5.0 g $NaNO_3$, 0.5 g $CaSO_4$ and 1 mg $(NH_4)_2MoO_4$. The 5% glucose was added after a series of preliminary measurements where 1, 3, 5 and 6% glucose was applied. Respiration was most uniform and had the smallest scatter when adding 5% glucose.

Measurements of soil respiration were made at 20°C and in the control container there was only the medium without soil. The measurements lasted 3 – 4 hours. Oxygen consumption was calculated after Klekowski (1975).

3. RESULTS

The data obtained show that soil moisture does not change much neither during the experiment nor between the variants, and is about 15% (Table 1). But the litter moisture, especially litter B, is higher and the scatter of results greater. This is probably due to the physical structure of the litter and thus various possibilities of retaining water.

The soil reaction is relatively high (pH over 6), but it is not possible to observe statistically significant changes due to acidification. The reaction of needles is of course lower, but changes during the acidification. In layer A, when sampling the material for the second time, i.e., after three months of acidification, the reaction differs significantly

Table 1. Soil moisture and acidity of two litter layers in experimental containers
A – undecomposed litter, B – partly decomposed litter

Date of sampling (1983)	Material	Moisture		pH	
		control % ± *S.D.* $n = 12$	acidified samples % ± *S.D.* $n = 12$	control ± *S.D.* $n = 12$	acidified samples ± *S.D.* $n = 12$
January 27	uncovered soil	15.38 ± 0.45	15.69 ± 0.70	6.68 ± 0.23	6.62 ± 0.17
	litter A	17.49 ± 4.09	17.36 ± 5.20	4.40 ± 0.02	4.44 ± 0.07
	litter B	37.06 ± 8.05	40.89 ± 7.48	4.98 ± 0.14	4.96 ± 0.09
	soil from under the litter	14.52 ± 0.56	14.80 ± 0.70	–	–
March 10	uncovered soil	15.26 ± 0.66	15.87 ± 0.52	6.41 ± 0.31	6.45 ± 0.18
	litter A	12.92 ± 1.25	21.10 ± 4.75	4.54 ± 0.05	4.45 ± 0.09
	litter B	32.39 ± 8.33	36.66 ± 7.93	5.03 ± 0.27	4.91 ± 0.10
	soil from under the litter	15.27 ± 0.80	14.63 ± 0.54	–	–
June 13	uncovered soil	14.69 ± 0.75	14.74 ± 0.81	6.34 ± 0.32	6.26 ± 0.32
	litter A	23.26 ± 4.55	28.35 ± 5.72	5.26 ± 0.11	5.03 ± 0.03
	litter B	36.23 ± 7.99	36.46 ± 4.06	4.72 ± 0.09	4.56 ± 0.07
	soil from under the litter	14.77 ± 1.19	15.33 ± 1.14	–	–

in the acidified and non-acidified series. Also the acidity of needles acidified for 6 months is statistically significantly lower at the third sampling of material (Table 1). In layer B the differences are statistically significant at the third sampling of material, i.e., 6 months after acidification. Thus when covering the soil with litter the pH reaction decreases and is more distinct in soil covered with litter than in that of black fallow type, the pH decreases in litter A after three months of acidification. These are not high values, but are statistically significant and there is a tendency of a decreasing environmental reaction.

The studies have shown that the level of organic matter and nitrogen compounds in soil under the litter is higher than in uncovered soil (Fig. 2). Also the ammonia nitrogen content in soils examined is higher in series acidified with solution of sulphuric acid than in control ones. Greater amounts of organic matter and nitrogen compounds under the litter prove first of all its fast – already at first sampling of material – effect upon soil fertility.

In the soil not covered with litter there are practically no differences in the organic matter content between the acidified and control series. The statistical significance of differences can be observed only during the third sampling in June (significance of differences 0.02). However, in the experiment with soil covered with litter the differences are statistically significant already at the second and, of course, at the third sampling. As shown in Figure 2, both at first and third sampling, the organic matter content in the acidified series is greater than in the control one, but at the second sampling the

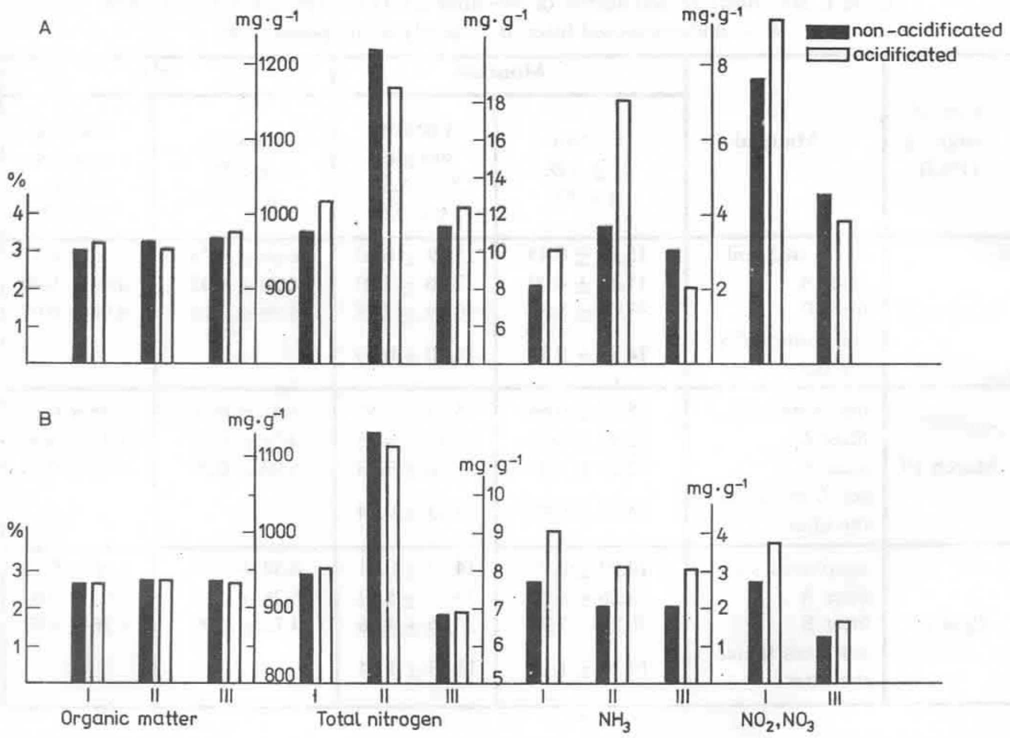

Fig. 2. The effect of environment acidification on the content of organic matter and nitrogen compounds in soil

A – soil under litter, B – soil not covered with litter, I – sampling one month after the experiment began (January 27), II – sampling after 2.5 months (March 10), III – sampling after 6 months (June 13)

differences are statistically insignificant. This may mean that the distribution of organic matter in soil is smaller in the acidified series, increasing the amounts or organic matter.

But this conclusion has not been confirmed directly by experiments on the organic matter decomposition rate in soil (Fig. 3). The decomposition is more intense in soil covered with litter than in that without it (Fig. 3). The differences are only statistically significant in the first series (soil without litter) for control and acidified series.

The decomposition rate in the acidified series is higher than in the non-acidified one. This is not consistent with data of other authors, but may be due either to accidental higher fertility of soil in acidified containers (not confirmed by organic matter and nitrogen content – Fig. 2) or to the first reaction of soil to an additional stimulus, in this case acidification.

However, from the ecological point of view the relative difference between the first and second period of investigations seems more important. The control series, both in soil with and without litter, shows a faster decomposition rate in the second period than in the first one. This is probably due to longer soil conditioning under laboratory conditions and thus to greater stability of soil system.

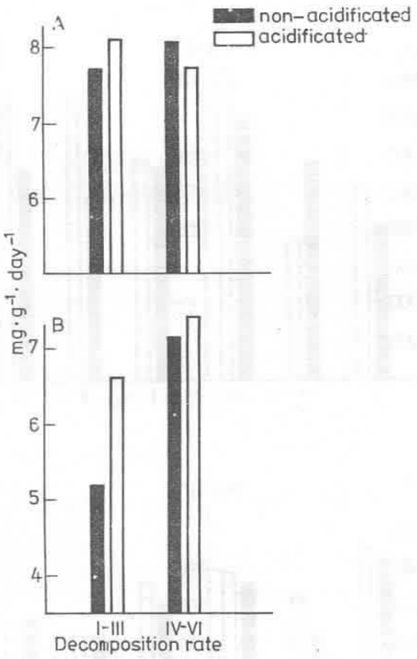

Fig. 3. The effect of environment acidification on the decomposition rate of organic matter measured by cellulose filter method

A and B – see Figure 2, I–III – exposure of filters in the three first months of experiment, IV–VI – exposure of filters in the next three months

In the control variant of the series with soil covered with litter the decomposition rate increases by about 5% (Table 2), i.e., at the second sampling it is some 5% faster than at the first one, whereas in the acidified series the decomposition rate at the second sampling is some 5% lower than at the first one. This regularity is more distinct in the variant without litter – the decomposition rate in the control increased by 38%, whereas in the acidified series – only 11%. Thus, considering the first experiment as an initial one in the acidified variant, the decomposition intensity is inhibited between January and June.

Table 2. Differences in the cellulose decomposition rate between the first and second period of investigations in per cents (100% decomposition rate in the first period)

Control		Acidified samples	
soil with litter	soil without litter	soil with litter	soil without litter
+4.95	+38.22	−5.30	+10.52

It is known that nitrification is inhibited by a too low soil reaction. This may even cause an increase in the amount of ammonia. Perhaps this is what happened in litter B as the level of nitrifying processes there is lower in acidified series (Fig. 4). At first

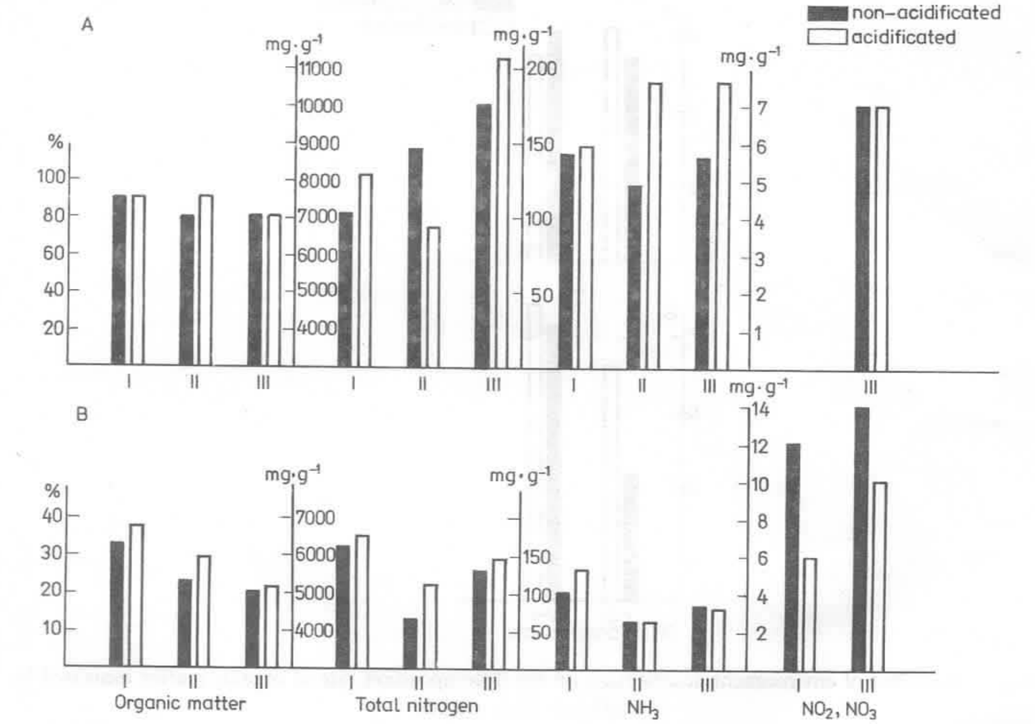

Fig. 4. The effect of environment acidification on the content of organic matter and nitrogen compounds in litter

A – undecomposed litter – equivalent of layer A_{OL}, B – litter having and advanced decomposition – equivalent of layer A_{OF}, I–III – see Figure 2

sampling in this litter the amount of ammonia has been higher in the acidified series, whereas at second and third sampling such differences have not observed. But the organic matter content in the acidified series (litter B) is always higher than in the non-acidified one. These differences are statistically significant (at 0.02 level) in series II only, but the general tendency is noticeable.

This tendency can be also observed in litter A, namely in the acidified series of the second sampling the organic matter content is higher than in the control (significance of differences 0.02).

As already mentioned the experiment has been controlled also by measuring sulphates in the water flowing out. There were no differences in non-acidified containers during the experiment (level of sulphates about 30 $mg \cdot l^{-1}$), whereas in acidified ones the content of sulphates increased during acidification (after 6 weeks 60 $mg \cdot l^{-1}$, after 6 months 90 $mg \cdot l^{-1}$ of liquid).

To obtain data on differences in the intensity of biological processes in soil examined, due to acidification of environment, oxygen consumption was measured using Kearney's medium. It was used to le ıe potential respiration of soil examined and the effect of acidification the indicatory investigations only one experimental variant was chosen – soil without litter directly affected by acid rain. Data on oxygen consumption together with standard error and deviation, averaged for a month series, indicated a lower metabolic level in acidified series (Fig. 5).

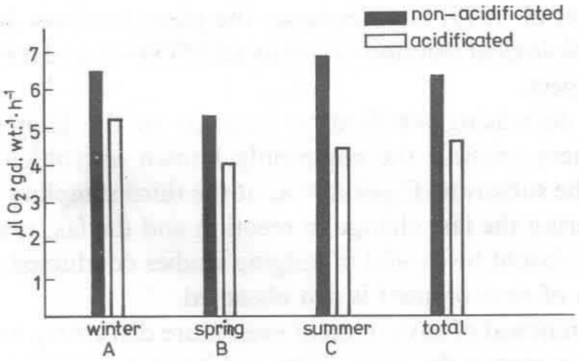

Fig. 5. The effect of environment acidification on the oxygen metabolism of soil measured by an indicatory method on Kearney's medium

A – material sampling 2 months after acidification began, B – material sampling 4 months after acidification began, C – sampling material 6 months after acidification began

Mean values of all measurements were calculated (Fig. 5). Differences in soil respiration of acidified and non-acidified soil were calculated for data each month and for all months. All tests showed high statistically significant differences among series examined. As seen in Figure 5, acidified soil had always a lower level of oxygen metabolism than the non-acidified one. It should be pointed out that differences between the respiration of acidified and non-acidified soil were similar in March and May (i.e., in spring), whereas in summer these differences were greater. And although the respiration level in acidified containers did not change much during the six months of the experiment, the level of metabolism increased in containers not acidified in summer.

This confirmed the results obtained using cellulose filters that showed the decomposition intensity. Thus, it had to be assumed that the intensity of ecological processes in the second experimental stage was higher than in the first one, and in this light the results should be examined. This could be due to long-lasting rating of specific ecological "equilibrium" of newly established system that had been previously destroyed or to the season of the year, i.e., summer and longer days.

4. DISCUSSION AND CONCLUSIONS

The differences in the intensity of basic ecological processes, such as soil metabolism, decomposition rate or nitrification, between series acidified for only 6 months and control ones, are surprising. The general opinion is that because the soil has strong buffering properties and does not change its reaction easily, the effect of acid rain on agricultural systems is almost unnoticeable.

There is a number of papers on the effect of acidification upon forests, which mainly blocks the decomposition of organic matter (Babich and Stotzky 1974, Coughtrey et al. 1979) and decreases the plant biomass. Not much has been written about the biological reaction of soil to acidification, and it mainly concerns the microbiological aspect.

Thus data on decreasing nitrification intensity in the litter and on increasing ammonification there confirm the commonly known microbiological reactions to changes in pH of the substrate. Especially as at the third sampling the pH of the litter decreases. Considering the fast change in reaction and the fast reaction of biological activity of soil one should be careful in judging studies conducted near power plants, where degradation of environment is not observed.

As regards the renewal of environment even more disturbing are data proving the inhibition of organic matter decomposition and intensity of soil oxygen metabolism, when pH does not decrease yet. Thus chemically the soil quality remains unchanged (no degradation), but the intensity of biological processes changes as well as the energy fluxes and next the matter. This is probably the beginning of the first stage of ecological degradation.

To some extent these results confirm the diagram of changes of the energy flow through soil system under the influence of power industry given by Fischer and Bieńkowski (1984) (Fig. 6). The amount of energy produced by the system as a result of metabolism of edaphon organisms (R) decreases and the decomposition is

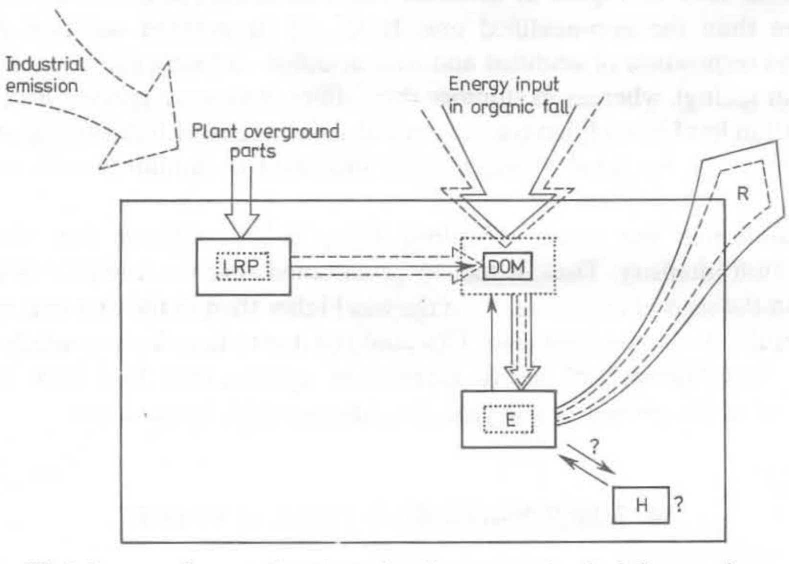

Fig. 6. Simplified diagram of energy flow through soil system under the influence of power industry Solid line – energy flow under natural conditions, dashed line – energy flow under conditions of industrial pressure, DOM – dead organic matter, E – edaphon, R – respiration, H – humus, LRP – live roots of plants (after Fischer and Bieńkowski 1984)

being inhibited. This process can be weaker when numbers of edaphon organisms or their activity change. Unpublished data of J. Szerszeń (personal communication), who has conducted parallel investigations, show a smaller number of bacteria after 6 months of acidification (before acidification $4.84 \cdot 10^7$, after – $3.12 \cdot 10^7$) and a higher number of fungi (before – $8.53 \cdot 10^4$, after – $10.79 \cdot 10^4$), i.e., a change in the structure of communities of microorganisms. Thus smaller activity of edaphon organisms may be not only due to its smaller numbers or activity, but also to changes in its structure.

The conclusions are:

At acidification of soil and soil covered with pine litter by water solution of sulphuric acid of a pH 3, noticeable changes in ecological processes can be observed already in six months' time and can indicate environmental degradation, namely:

(1) Inhibition of nitrification in the fermentation litter layer (litter B).
(2) Increase of organic matter in the litter.
(3) Increasing intensity of ammonification in the surface litter (B).
(4) Inhibition of organic matter decomposition.
(5) Inhibition of intensity of oxygen metabolism of soil.

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5. SUMMARY

The effect of acidification on soil in a black fallow and on soil covered with pine needle litter has been investigated in a laboratory experiment (Fig. 1). The soil was acidified for 6 months with water solution of sulphuric acid of a pH 3. The intensity of metabolism, contents of organic matter and various nitrogen compounds and decomposition rate measured by cellulose filter method were treated as indices of biological activity of the environment examined.

No statistically significant differences in acidification were observed in the soil remaining in the black fallow, whereas in soil covered with litter pH reaction decreased as compared with the control (Table 1). In the fermentation litter layer the organic matter content increased under the influence of acidification, and nitrification was inhibited (Fig. 4). Simultaneously, the intensity of ammonification increased in the surface litter layer. An analysis of the decomposition rate of cellulose filters indicated an inhibition of organic matter decomposition (Table 2). Also under the influence of acidification, oxygen metabolism of soil decreased significantly (Fig. 5).

6. POLISH SUMMARY

Z pomocą eksperymentu laboratoryjnego (rys. 1) badano wpływ zakwaszenia na glebę pozostawioną w czarnym ugorze oraz glebę pokrytą ściółką sosnową. Glebę zakwaszano roztworem wodnym kwasu siarkowego o pH 3. Zakwaszenie trwało 6 miesięcy. Jako wskaźniki aktywności biologicznej badanego środowiska przyjęto: intensywność procesów metabolicznych, zawartość substancji organicznej i różnych form azotu oraz szybkość rozkładu mierzoną wskaźnikową metodą sączków celulozowych.

W glebie pozostawionej w czarnym ugorze nie stwierdzono statystycznie istotnych różnic w zakwaszeniu, natomiast w glebie pokrytej ściółką odczyn pH obniża się w porównaniu z kontrolą (tab. 1). W warstwie ściółki fermentacyjnej pod wpływem zakwaszenia zanotowano wzrost zawartości materii organicznej oraz hamowanie procesów nitryfikacyjnych (rys. 4). Równocześnie w warstwie ściółki powierzchniowej stwierdzono wzrost intensywności procesów amonifikacyjnych. Analiza tempa rozkładu sączków celulozowych wskazuje na hamowanie procesów rozkładu materii organicznej (tab. 2). Stwierdzono również, że pod wpływem zakwaszania obniża się istotnie metabolizm tlenowy gleby (rys. 5).

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